

PATENT  
SOLU:113  
14-54(8992)



APPLICATION FOR UNITED STATES LETTERS PATENT

for

PROCESS FOR NITROUS OXIDE PURIFICATION

by

J. P. OPPENHEIM, PATRICK NOTTE, ALEXANDER NOSKOV,  
BARRY BOWMAN, RAMOORTHY CHANDRASEKHAR AND  
GREG CROCE

EXPRESS MAIL MAILING LABEL	
NUMBER	<u>EL 291391777US</u>
DATE OF DEPOSIT	<u>5-26-99</u>
I hereby certify that this paper or fee is being deposited with the United States Postal Service "EXPRESS MAIL POST OFFICE TO ADDRESSEE" service under 37 C.F.R. 1.10 on the date indicated above and is addressed to: Assistant Commissioner for Patents, Washington D.C. 20231.	
<u>Maria L. Alvarez</u>	
Signature	

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29

**FIELD OF THE INVENTION**

The present invention relates to a process for purifying a nitrous oxide gas by removal of various impurities.

**BACKGROUND OF THE INVENTION**

A number of processes for purification of off-gases and exhaust gases produced from various thermal power plants are known in the art. Such gases contain undesirable components, such as NOx (nitrogen oxides including NO, N<sub>2</sub>O<sub>3</sub>, NO<sub>2</sub>, N<sub>2</sub>O<sub>4</sub>, N<sub>2</sub>O<sub>5</sub>, etc.), sulfur oxides, and the like. These processes are based either on absorption of such impurities by liquid absorbents, or on their conversion (reduction) into harmless compounds (e.g., water vapor and nitrogen in the case of NOx reduction). The most widely employed processes for reduction of NOx use ammonia and selective catalytic reduction (SCR). The SCR processes make it possible to carry out the reduction of NOx to elemental nitrogen and water vapor in the presence of oxygen contained in the off-gases. See U. S. Patents Nos. 5,401,479; 4,859,439; 4,855,115; 4,789,533; 4,438,082; 4,720,476; 4,695,438; 4,732,743; 4,975,256; 4,521,388; 5,401,478; and 5,753,582, the entire subject matter of which is incorporated herein by reference. After off-gases are cleaned of minor impurities by conventional processes/equipment, they are vented to the atmosphere.

Moreover, there are also known processes for purifying various commercial grade gases, such as inert gases. For example, U. S. Patent No. 4,579,723, the entire subject matter of which is incorporated by reference, utilizes a multi-step catalytic process to remove CO, CO<sub>2</sub>, H<sub>2</sub>, H<sub>2</sub>O, and O<sub>2</sub> from an argon gas.

Various processes have been utilized for removing O<sub>2</sub> from very pure nitrous oxide gas produced from stand alone commercial processes for subsequent use in semiconductor manufacturing. In Japanese Kokai No. 06016402, oxygen is removed from commercially produced nitrous oxide using a manganese oxide catalyst. However, oxygen is removed by using oxygen present in the gas to oxidize the catalyst from a

1 lower to a higher manganese oxide, which does not involve catalysis of reactions  
2 involving oxygen containing gases to form easily removed products.

3 Heretofore, removal of impurities from nitrous oxide off-gases has not been  
4 contemplated. Releasing nitrous oxide off-gases into the environment is a source of  
5 pollution and a waste of nitrous oxide that, if economically and feasibly separated from  
6 such off-gases to provide a commercial grade nitrous oxide source, could lead to its use in  
7 various processes, such as for use in conversion of benzene to phenol by hydroxylation.  
8 See U. S. Patents Nos. 4,982,013; 5,001,280; 5,055,623; 5,110,995; 5,672,777; 5,756,861  
9 and 5,808,167, the entire subject matter of which is incorporated herein by reference.  
10 Accordingly, there is a need in the chemical industry for a process that purifies nitrous  
11 oxide off-gases and at the same time commercially and economically produces nitrous  
12 oxide suitable for various commercial applications.

### 14 SUMMARY OF THE INVENTION

15 The present invention relates to a method for purification of a nitrous oxide gas by  
16 feeding the nitrous oxide gas and reducing agent or precursor thereof into a de-oxidation  
17 reactor, and performing de-oxidation by reacting the reducing agent or precursor thereof  
18 with oxygen using a catalyst to form an inert, in order to deplete the oxygen in the nitrous  
19 oxide gas, while limiting the amount of nitrous oxide removed from the nitrous oxide gas.

20 Additionally, the present invention concerns a method for purification of a nitrous  
21 oxide gas by feeding the nitrous oxide gas and ammonia or a precursor thereof into a  
22 reactor system, performing selective catalytic reduction by reacting the ammonia or  
23 precursor thereof with NO<sub>x</sub> in the nitrous oxide gas using a selective catalytic reduction  
24 catalyst, feeding hydrogen or a precursor thereof into the reactor system and performing  
25 de-oxidation by reacting the hydrogen or a precursor thereof with oxygen in the nitrous  
26 oxide gas using a de-oxidation catalyst.

### 28 BRIEF DESCRIPTION OF THE DRAWINGS

29 The present invention will be more clearly understood by reference to the  
30 following description of exemplary embodiments thereof in conjunction with the attached

1 drawings, which represent data obtained as a result of an embodiment of a process  
2 according to the invention as set forth in EXAMPLES I and II.

### 3 4 **DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS**

5 In accordance with the present invention, a nitrous oxide off-gas is purified  
6 utilizing catalytic processes to provide an economical source of nitrous oxide suitable for  
7 various commercial applications. Moreover, the process of the present invention  
8 selectively purifies nitrous oxide off-gas while maintaining the amount of nitrous oxide in  
9 the off-gas by selectively reacting out selected impurities in the off-gas. Such a purified  
10 nitrous oxide off-gas may be utilized in one-step hydroxylation of benzene to phenol, as  
11 set forth in U. S. Patents Nos. 4,982,013; 5,001,280; 5,055,623; 5,110,995; 5,672,777;  
12 5,756,861 and 5,808,167, the entire subject matter of which is incorporated herein by  
13 reference.

14 In one embodiment of the present invention, nitrous oxide off-gas is passed  
15 through an SCR reactor in the presence of ammonia or a precursor thereof to remove  
16 (e.g., by reacting) NO<sub>x</sub> while at the same time not reducing the amount of nitrous oxide  
17 in the off-gas. The reactor comprises at least one catalyst bed and may be of any suitable  
18 configuration such as fixed bed reactor, (e.g., metal, parallel plate, ceramic honeycomb,  
19 tubular, or a lateral flow reactor). Preferably, the reactor is a lateral flow reactor. A  
20 lateral flow reactor allows a pellet type of catalyst to be employed in a fixed bed  
21 providing a higher contact efficiency at a lower pressure drop than a honeycomb catalyst  
22 in the same service. Intimate mixing between the ammonia vapor and process gas is  
23 accomplished with the use of perforated plates.

24 The catalyst may comprise any known NO<sub>x</sub> abatement SCR catalyst, such as  
25 those based on transition metals, e.g., Ti, V, W, Mo, Mn, Cu, Fe, Cr, Co, Ni, Zn, Sn, etc.  
26 The metal may be in the form of an oxide and may be integrated with or placed on a  
27 conventional carrier, such as silica and/or alumina. Preferably, an oxide of Ti-V catalyst  
28 is used.

29 The catalyst pellets may be formed into any shape, such as cylinders, spheres,  
30 discs, rings, etc., or in the form of a honeycomb block and utilized under conventional

1 SCR conditions. These conditions are dictated by the space velocity of the catalyst, its  
2 operating temperature, and the NOx loading.

3 For example, ammonia or a precursor thereof is mixed with the nitrous oxide off-  
4 gas containing NOx at a molar ratio with respect to the NOx from 0.1 to 2.0, preferably  
5 0.5 to 1.5, and more preferably from 0.8 to 1.2. The mixture may be at a temperature  
6 from 100°C to 600°C, preferably from 120°C to 400°C, and more preferably from  
7 150°C to 300°C. For adipic acid off-gas service where nitrous oxide is to be preserved,  
8 a low temperature range between 150 to 350°C is preferable. Space velocities (amount  
9 of gas in cubic meters that passes in one hour through one cubic meter of the catalyst  
10 (apparent volume of the catalyst bed) stated with the dimension reciprocal hour) in the  
11 range from 300 to 100,000 h<sup>-1</sup> may be utilized. The process may be conducted under any  
12 pressure. However suitable pressures range from about 1 to about 10 atmospheres.

13 The ammonia or precursor thereof reacts with the NOx to form N<sub>2</sub> and H<sub>2</sub>O. The  
14 nitrous oxide exiting the reactor comprises less than 200 ppm of NOx, preferably less  
15 than 40 ppm, and more preferably less than 10 ppm.

16 Prior to entering the reactor, ammonia and a carrier gas are mixed together. The  
17 carrier gas may contain any inert gas that does not significantly deactivate the catalyst.  
18 For example, the carrier gas may contain steam, hydrogen, argon, etc., or mixtures  
19 thereof. Preferably the carrier gas contains steam.

20 In another embodiment of the present invention, nitrous oxide off-gas is passed  
21 through at least one reactor in the presence of a reducing agent or precursor thereof and a  
22 catalyst to remove oxygen and other impurities, such as organics (e.g., CO, etc.) without  
23 reducing the amount of nitrous oxide present in the off-gas. The reactor comprises at  
24 least one catalyst bed and may be of any suitable configuration such as a fixed bed, a  
25 tubular reactor, or a lateral flow reactor. Preferably, the reactor is a fixed bed reactor.

26 The catalyst may comprise any known oxidation catalyst, such as those based on a  
27 noble metal or combination of noble metals (e.g., platinum or palladium, etc.). The  
28 catalyst may be integrated with or placed on a conventional carrier, such as silica and/or  
29 alumina. Preferably, the catalyst is a palladium metal with an alumina support.

1           The catalyst may be formed into any shape, such as cylinders, spheres, discs,  
2 rings, etc., or in the form of a honeycomb block. Preferably, the catalyst is in the form of  
3 a honeycomb block.

4           In this embodiment of the present invention, stoichiometric amounts of a reducing  
5 agent or precursor thereof is mixed with the nitrous oxide off-gas containing oxygen.  
6 The mixture may be at a temperature from 0°C to 600°C, preferably from 5°C to  
7 300°C, and more preferably from 10°C to 200°C. Space velocities (amount of gas in  
8 cubic meters that passes in one hour through one cubic meter of the catalyst (apparent  
9 volume of the catalyst bed) stated with the dimension reciprocal hour) in the range from  
10 300 to 100,000 h<sup>-1</sup> may be utilized. The process may be conducted under any pressure.  
11 However suitable pressures range from about 1 to about 10 atmospheres.

12           The reducing agent or precursor thereof may be mixed with the nitrous oxide off-  
13 gas prior to entering the reactor, or in the reactor itself. This may be accomplished using  
14 conventional means, such as an inline mixer. Suitable reducing agents include agents that  
15 selectively react with oxygen in the nitrous oxide off-gas without depleting the nitrous  
16 oxide in the off-gas. For example, the reducing agent may be hydrogen, which  
17 selectively reacts (using an appropriate catalyst as described herein) with oxygen present  
18 in the off-gas to produce water. In an embodiment of the present invention, it has been  
19 discovered that the hydrogen unexpectedly does not deplete the nitrous oxide in the off-  
20 gas (hydrogen would have been expected to also react with nitrous oxide to form nitrogen  
21 and water. Another suitable reducing agent is, for example, carbon monoxide, which  
22 selectively reacts with oxygen to form carbon dioxide without depleting the nitrous oxide  
23 present in the off-gas. The reducing gas may contain a mixture of gases, such as  
24 hydrogen and carbon monoxide. Preferably, the reducing gas is a hydrogen containing  
25 gas. The hydrogen may be provided in any form, including any hydrogen containing gas  
26 such as hydrogen plant offgas, offgas from a dehydrogenation process (e.g. ethylbenzene  
27 to styrene), etc. Preferably, the hydrogen is provided in the form of pure hydrogen.

28           In another embodiment of the present invention, the nitrous oxide off-gas is  
29 passed through an SCR reactor to remove NO<sub>x</sub> utilizing the NO<sub>x</sub> abatement process of  
30 the present invention and subsequently the nitrous oxide off-gas is passed through a de-

1 oxidation reactor to remove oxygen and other impurities using the de-oxidation process  
2 of the present invention. Alternatively, the de-oxidation process may precede the NOx  
3 abatement process. Moreover, such processes may be conducted multiple times and in  
4 any order. The NOx abatement and de-oxidation processes may be conducted in a single  
5 reactor having multiple catalyst beds or in a single reactor having multiple chambers.  
6 Additionally, each of the NOx abatement and de-oxidation processes may be conducted  
7 utilizing multiple reactors. Preferably, NOx abatement precedes de-oxidation.

8 The recovery of nitrous oxide from the nitrous oxide off-gas utilizing the present  
9 purification system comprises greater than 50%, preferably greater than 70%, and more  
10 preferably greater than 95%.

## 11 EXAMPLES

12 Processes of the present invention are further defined by reference to the  
13 following illustrative examples.  
14

### 15 EXAMPLE I

16 A process for purification of a nitrous oxide gas of the present invention is  
17 performed as follows:  
18

19 A 0.2% w/w Pd on alumina catalyst in the form of beads from Johnson-Matthey is  
20 exposed to a gas stream of 60 cc/min composed of 2.4 cc/min of oxygen, 36 cc/min of  
21 nitrous oxide, and 6 cc/min of helium at 150°C in a quartz reactor. Contact time is 4.6  
22 seconds. Part of the helium gas is gradually replaced by pure hydrogen. Reaction is  
23 followed up by analysis of the reactor effluent by mass spectrometry (amu 32 for oxygen,  
24 amu 28, 30 and 44 for nitrous oxide, amu 2 for hydrogen, amu 18 for water). Complete  
25 reaction of hydrogen is observed in all the tested cases. Figures 1 and 2 illustrate the  
26 selective reaction of oxygen with hydrogen, and not with nitrous oxide, respectively.  
27 Figure 1 shows the oxygen destruction as a function of the hydrogen flow. Figure 2  
28 demonstrates the percent nitrous oxide destruction as a function of the hydrogen flow.  
29 Figure 3 represents the oxygen destruction selectivity as a function of the hydrogen flow.  
30

**1**

2

## 9

10

## 15

16

18